colorless prisms had mp 189-190°C (from alcohol with ethyl acetate). Found %: C 62.5; H 6.3; Cl 14.1; N 17.0. $C_{13}H_{15}N_3 \cdot HCl$. Calculated %: C 62.4; H 6.4; Cl 14.2; N 16.8.

2-Phenyl-4-methylpyrazolo[1,5-a]benzimidazole (VIe). A mixture of 0.5 g (1.4 mmole) of IVe in 30 ml of concentrated HCl and 10 ml of alcohol was refluxed for 40 h, after which it was cooled, and 0.3 g (60%) of starting compound was removed by filtration. Workup of the filtrate after neutralization with 22% NH_4OH gave 0.15 g (40%) of colorless needles of VIe with mp 98-100°C (from alcohol). Found %: C 77.5; H 5.1; N 16.8. $C_{16}H_{13}N_3$. Calculated %: C 77.7; H 5.3; N 17.0.

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SYNTHESIS, STRUCTURE, AND TAUTOMERISM OF FORMAZANS THAT CONTAIN 1-ARYL-2-BENZIMIDAZOLYL RESIDUES

G. N. Tyurenkova, I. I. Mudretsova, S. L. Mertsalov, and N. P. Bednyagina

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1,5-Bis(1-aryl-2-benzimidazolyl)-3-methyl- and 1-(p-tolyl)-3-methyl-5-(1-aryl-2-benzimidazolyl)formazans were synthesized. It was shown by IR spectroscopy (from the change in the spectral characteristics of the NH groups) that the formazans exist in the imino form in solutions in CCl_4, whereas a tautomeric equilibrium between the amino and imino forms of the investigated compounds is observed in solutions in $CHCl_3$.

It has been shown [1] that formazans that contain 1-alkyl- or 1-benzyl-2-benzimidazolyl groups in the 1(5) position exist in the open imino form, regardless of the substituent (methyl or phenyl) in the 3 position. The localization of the proton attached to the heterocyclic nitrogen atom in benzimidazolylformazans was explained by the considerable basicity of the benzimidazole ring. In [2] it was demonstrated experimentally that, depending on the character of the ring and the medium, hydrazones with various benzazolyl substituents can exist in a state of tautomeric amino—imino equilibrium.

It is known [3, 4] that the introduction of a phenyl group in the 1 position decreases the basicity of imidazole and benzimidazole. Proceeding from this, one might have expected that the amino form could also be observed for N-phenyl-substituted formazans in the equilibrium of tautomeric forms. The introduction of an ortho substituent will give rise to still greater noncoplanarity of the phenyl group [5] and will increase the shift of the equilibrium to favor the amino form.

In this connection, we synthesized a group of unsymmetrical (Ia-c) and symmetrical (IIa-c) formazans:

S. M. Kirov Ural Polytechnic Institute, Sverdlovsk 620002.

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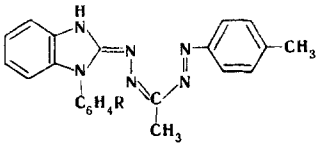
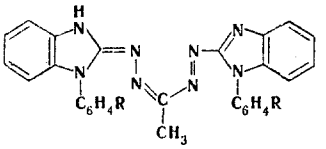
TABLE 1. IR Spectra of I and II

Compound	In CCl_4		In $CHCl_3$		
	ν, cm^{-1}	$\Delta\nu_{1/2}$, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}	$\Delta\nu_{1/2}$, cm^{-1}
Ia	3438	22,0	3438	3336 w	34,0
Ib	3441	22,5	3440	3333 w	34,0
Ic	3439	22,0	3438	3332 w	34,0
IIa	3427	22,5	3406	3286 w	33,5
IIb	3430	24,0	3410	3287 w	33,0
IIc	3428	25,0	3408	3287 w	34,5



I a-c



II a-c

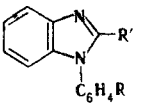
a R = H, b R = OCH_3-2; c R = OCH_3-4

Compounds I are the products of coupling of a p-toluenediazonium salt with 1-aryl-2-acetaldehydehydrazonobenzimidazoles. Formazans II were obtained by autooxidation of the corresponding hydrazines. In the preparation of formazan Ia diazo coupling was carried out without isolation of the hydrazone, while in the synthesis of Ib, c substances that were obtained and isolated as the hydrazones were subjected to the reaction. However, the products of the reaction of acetaldehyde with 1-(o- and p-anisidyl)-2-hydrazinobenzimidazoles are not in agreement with the expected structures, since their IR spectra do not contain the absorption bands of NH groups. Data on the structures of these compounds will be published later.

Only one high-frequency absorption band is observed in the IR spectra of freshly prepared solutions of I and II in CCl_4 (Table 1), and this, according to [1, 2], constitutes evidence for the existence of the formazans in the imino form. The IR spectra were recorded under conditions that exclude the self-association of the formazans. The integral intensities of the NH bands are sensitive to structural changes. The degree of polarization of the NH bond in Ib is the least polar NH bond in a series of unsymmetrical formazans. The methoxy group in the ortho position of the phenyl ring leads to a decrease of ~ 30% in the integral intensity as compared with formazan Ia ($8.1 \cdot 10^3$ and $1.2 \cdot 10^4$ liters/mole-cm^2, respectively). This effect is not observed if the methoxy group is in the para position (Ic) (the relative integral intensity is $1.22 \cdot 10^4$ liters/mole-cm^2). A substituent in the ortho position gives rise to additional deviation of the phenyl ring [5] from conjugation with the benzimidazole ring, and this leads to a certain degree of strengthening of the NH bond and a decrease in its polarity.

The numerical values of the relative integral intensities that characterize the NH bonds symmetrical formazans IIa-c are $5.5 \cdot 10^3$, $7.4 \cdot 10^3$, and $5.0 \cdot 10^3$ liters/mole-cm^2, respectively. In addition to the certain amount of weakening of the NH bond, the decrease in its polarity as compared with the polarity in unsymmetrical formazans may be associated with the competitive effect of a grouping in the 1 position of the formazan ring that has a similar basicity, which causes a decrease in the basicity and an increase in the lability of the proton in the 5 position of the benzimidazole ring. Another piece of evidence for an increase in the proton-donor capacity of the heteroring of symmetrical formazans as compared with unsymmetrical formazans is the ~ 20 cm^{-1} decrease in the absorption frequency of the high-frequency band of the NH bond of IIa-c in the IR spectra of chloroform solutions (Table 1). A change in the ratio of the basicities of the ring and exocyclic nitrogen atoms in favor of the latter occurs in the more polar chloroform, and a prototropic tautomeric transition therefore becomes possible, which also explains the appearance of the weak but distinct absorption of the amino form with a maximum at ~ 3340 cm^{-1} in the spectra of chloroform solutions of all of the investigated formazans.

Thus, in the benzimidazolylformazan series the introduction of an aryl residue in the benzimidazole ring in place of an alkyl or aryl residue shifts the imine $\rightleftarrows$ amine tautomeric equilibrium to favor the amino form, although the contribution of the latter is small and is observed only in a polar solvent.

TABLE 2. 1-Arylbenzimidazole Derivatives 

R	R′	mp. °C	Found, %		Empirical formula	Calc., %	
			N	S		N	S
H	SCH_3	56—60 [7]	—	—	—	—	—
2-OCH_3	SCH_3	101—103	10,8	12,3	$C_{15}H_{14}N_2OS$	10,4	11,9
4-OCH_3	SCH_3	140—142	10,3	11,5	$C_{15}H_{14}N_2OS$	10,4	11,9
H	SO_2CH_3	136—137	10.2	—	$C_{14}H_{12}N_2O_2S$	10,3	—
2-OCH_3	SO_2CH_3	128—130	9,5	11,0	$C_{15}H_{14}N_2O_3S$	9,3	10,6
4-OCH_3	SO_2CH_3	159—160	9,7	10,2	$C_{15}H_{14}N_2O_3S$	9,3	10,6
H	$NHNH_2$	150—152	25,4	—	$C_{13}H_{12}N_4$	25,0	—
2-OCH_3	$NHNH_2$	141—143	21,5	—	$C_{14}H_{14}N_4O$	22,0	—
4-OCH_3	$NHNH_2$	165—167	21,9	—	$C_{14}H_{14}N_4O$	22,0	—

TABLE 3. Formazans (I and II) of the 1-Arylbenzimidazole Series

Compound	mp, °C	Spectra in the visible region (alcohol), λ_{max}, nm (log ε)	Found, %			Empirical formula	Calc., %			Yield, %
			C	H	N		C	H	N	
Ia	99—100	452 (4,46)	70,2	5,4	22,3	$C_{22}H_{20}N_6 \cdot 1/2H_2O$ [a]	70,0	5,5	22,3	80
Ib	95—97	460 (4,38)	69,6	5,7	—	$C_{23}H_{22}N_6O$ [b]	69,3	5,6	—	53
Ic	181—183	455 (4,32)	69,5	5,6	—	$C_{23}H_{22}N_6O$	69,3	5,6	—	92
IIa	152—158	539 (4,61)	66,1	5,0	22,6	$C_{28}H_{22}N_8 \cdot 2H_2O$	66,4	5,1	22,1	28
IIb	155—157	534 (4,62)	67,5	5,1	21,9	$C_{30}H_{26}N_8O_2$ [c]	67,9	4,9	21,1	30
IIc	229—231	543 (4,60)	63,9	5,0	19,6	$C_{30}H_{26}N_8O_2 \cdot 2H_2O$	63,6	5,3	19,8	30

[a]Found %: H_2O 3.2. Calculated %: H_2O 2.6. [b]After drying over P_2O_5 at 70°C; crystallized with 0.5 mole of H_2O. Found %: H_2O 2.4. Calculated %: H_2O 2.2. [c]After drying over P_2O_5 at 70°C crystallized with 2 moles of H_2O. Found %: H_2O 6.1. Calculated %: H_2O 6.6.

EXPERIMENTAL

The electronic spectra of 10^{-4} M solutions of the compounds were recorded with a Specord UV-vis spectrophotometer. The IR spectra of $2 \cdot 10^{-4}$-$4 \cdot 10^{-4}$ M solutions in CCl_4 and $5 \cdot 10^{-4}$-$1 \cdot 10^{-3}$ M solutions in $CHCl_3$ in 50- and 20-mm thick layers, respectively, were recorded with a UR-20 IR spectrometer. The relative integral intensities were measured by the Wilson—Welles method, and the areas under the contours of the absorption curves were calculated from the Simpson formula.

1-Aryl-2-methylmercaptobenzimidazoles. A 10-ml sample of methyl iodide was added to a mixture of 0.5 mole of the corresponding thione in 50 ml of ethanol and 15 ml of 30% NaOH solution, and the mixture was allowed to stand at room temperature for 24 h with periodic stirring. Water was added, and the liberated oil began to crystallize gradually. The products were obtained in 80-90% yields (Table 2).

2-Aryl-2-benzimidazolyl Methyl Sulfones. These compounds were obtained in 60-70% yields by oxidation of the corresponding sulfides in acetic acid with 7% potassium permanganate solution as in [6] (Table 2).

1-Aryl-2-hydrazinobenzimidazoles. These compounds were obtained in 80-90% yields from the corresponding sulfones by the method in [7] and were crystallized from aqueous ethanol (without charcoal).

1-(p-Tolyl)-3-methyl-5-(1-aryl-2-benzimidazolyl)formazans (Ia-c). A 3-ml sample of acetaldehyde was added to a suspension of 4 mmole of 1-aryl-2-hydrazinobenzimidazole in 10 ml of ethanol, and the mixture was heated on a water bath for 30 min (in the case of Ia) or until a precipitate formed (in the case of Ib, c), after which it was cooled, and the precipitate was removed by filtration and crystallized [from dimethylformamide (DMF) in the case

of Ib (mp 245°C) or form aqueous ethanol in the case of Ic (mp 235-237°C)]. The alcohol solution (in the preparation of Ia) was cooled to 0°C, 3 ml of a 30% solution of sodium hydroxide was added, and coupling with p-toluenediazonium chloride (from 4.2 mmole of p-toluidine in 10 ml of 2 N HCl and 4.5 mmole of sodium nitrite) was carried out while maintaining the pH of the medium at 9-10. At the end of the addition of the diazonium salt, the reaction mixture was maintained at 0°C for 1 h, after which it was carefully neutralized with hydrochloric acid solution, and the precipitate was removed by filtration. Compounds Ib, c were similarly obtained. Coupling was carried out at 0°C, and the reaction mixture was allowed to stand for 24 h. In the case of Ib DMF was used as the solvent. Formazans Ia-c were crystallized from ethanol or ethanol—water (Table 3).

1,5-Bis(1-aryl-2-benzimidazolyl)-3-methylformazans. These compounds were obtained as dark crystals with a metallic luster by autooxidation in ethanol in the presence of sodium acetate (Table 3).

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TAUTOMERISM OF AZINE DERIVATIVES. 4.* KETO-ENOL TAUTOMERISM OF β-KETO ESTERS OF THE AZINE SERIES

S. A. Stekhova, O. A. Zagulyaeva, V. V. Lapachev, and V. P. Mamaeva

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The structures of pyrazinoyl-, 3-pyridazinoyl-, 4-pyrimidoyl-, and 2-, 3-, and 4-pyridoylacetic esters were studied by means of IR, NMR, and ^1H and ^{13}C NMR spectroscopy and quantum-chemical calculations (Pariser—Parr—Pople and CNDO/2). The effect of solvents (including strongly and weakly basic solvents) on the position of the tautomeric equilibria of these β-keto esters was studied. The σ^+ constants for the keto and enol fragments were estimated by means of quantum-chemical calculations and ^{13}C NMR spectroscopy.

Little study has been devoted to the tautomerism of azine analogs of β-dicarbonyl compounds of the benzene series [2-4], although the presence of a heteroatom that is capable of forming a hydrogen bond and undergoing protonation may have a substantial effect on the structures of the tautomeric forms and on the position of the equilibrium between them.

In the present research we studied the tautomerism of aza analogs of benzoylacetic esters (I-VI) in various solvents.

Compounds I-VI, together with the previously described 2-pyrimidoyl [2] and 4-pyridazinoylacetic [3] esters, represent a series of azinoylacetic esters that contain most of the possible combinations of one or two nitrogen atoms in the ring with respect to the tautomeric

*See [1] for communication No. 3.

Novosibirsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Novosibirsk 6300090.

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